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TITLE: Conformal thin films over textured capacitor electrodes

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Summary of Invention Paragraph - BSTX (14):

[0012] Referring to FIG. 3, an enlarged view of an HSG silicon layer 50 is illustrated. The layer 50 comprises hemispherical grains 52 of conductively doped polycrystalline silicon (polysilicon, or simply poly) over a conductive substrate 54. The grains 52 have grain sizes ranging from about 50 .ANG. to about 750 .ANG.. A dielectric layer 56, deposited by CVD, is shown over the HSG layer 50. The illustrated dielectric comprises conventional dielectric materials, such as silicon oxide (SiO.sub.2) and/or silicon nitride (Si.sub.3N.sub.4), which are well-understood and easily integrated with conventional fabrication process flows. CVD processes for these materials, for example, are well developed.

Summary of Invention Paragraph - BSTX (15):

[0013] As shown, the dielectric layer 56 deposited by CVD is relatively conformal over the surfaces of the HSG silicon layer 50. However, conventional CVD processes cannot produce perfectly conformal dielectrics over high surface area textures, such as HSG silicon, due to a variety of factors. CVD inherently results in disparate deposition rates at different points of the topography across the workpiece. Non-uniformities in temperature across a workpiece, particularly across large workpieces like 300-mm wafers, can strongly influence thickness uniformity of a CVD layer. Variations in reactant concentration, due to reactor design, gas flow dynamics and the depletion effect, similarly affect the thickness uniformity across large workpieces. Due to these and other problems, growth rates and conformality cannot be controlled with absolute precision using conventional CVD.

Summary of Invention Paragraph - BSTX (18):

[0016] Due in part to such limitations on capacitance enhancement by increasing electrode surface area, more recent attention has been focused instead upon methods of increasing the dielectric constant (k) of the capacitor

dielectric. Much effort has been aimed at integrating new dielectric materials having higher k values. High k materials include aluminum oxide (Al.sub.2O.sub.3), tantalum oxide (Ta.sub.2O.sub.5), barium strontium titanate (BST), strontium titanate (ST), barium titanate (BT), lead zirconium titanate (PZT), and strontium bismuth tantalate (SBT). These materials are characterized by effective dielectric constants significantly higher than conventional dielectrics (e.g., silicon oxides and nitrides). Whereas k equals 3.9 for silicon dioxide, the dielectric constants of these new materials can range from on the order of 10 (aluminum oxide) to 300 (BST), and some even higher (600 to 800). Using such materials enables much greater increases in cell capacitance/footprint.

Summary of Invention Paragraph - BSTX (20):

[0018] Integrating high k materials into conventional process flows, however, has proven challenging. Some materials, such as Ta.sub.2O.sub.5, BST and other "exotic" materials, tend to involve highly oxidizing, high temperature deposition and post-deposition anneal conditions, leading to oxidation of traditional electrode materials and even diffusion of oxygen into lower circuit elements. Other materials, such as ZrO.sub.2 and TiO.sub.2, have highly inconsistent properties, depending upon a variety of processing conditions.

Detail Description Paragraph - DETX (6):

[0041] The preferred embodiments provide exemplary processes for depositing Al.sub.2O.sub.3 (k .apprx.10), ZrO.sub.2 (k.apprx.12-20), TiO.sub.2 (k.apprx.20-50), mixed zirconium silicon oxide (k.apprx.8-13), and nanolaminate dielectrics formed by combinations of the above. Similarly, methods are provided for depositing electrode materials over the dielectric and HSG silicon. These materials are all formed by methods compatible with HSG silicon, furthermore producing almost perfect conformality. Thus, the preferred embodiments allow increased capacitance not only due to the high k dielectric materials, but also due to taking full advantage of the increased surface area afforded by HSG silicon. Such conformality obtains even over high aspect ratio structures like stacked and trench capacitor designs.

Detail Description Paragraph - DETX (9):

[0044] FIG. 4A generally illustrates a method of forming capacitor dielectric layers with high step coverage. The preferred method is a form of atomic layer deposition (ALD), whereby reactants are supplied to the workpiece in alternating pulses in a cycle. Preferably, each cycle forms no more than about one monolayer of material by adsorption and more preferably by chemisorption. The substrate temperature is kept within a window facilitating

chemisorption. In particular, the substrate temperature is maintained at a temperature low enough to maintain intact bonds between adsorbed complex and the underlying surface, and to prevent decomposition of the precursors. On the other hand, the substrate temperature is maintained at a high enough level to avoid condensation of reactants and to provide the activation energy for the desired surface reactions in each phase. Of course, the appropriate temperature window for any given ALD reaction will depend upon the surface termination and reactant species involved.

Detail Description Paragraph - DETX (15):

[0050] Within the preferred reactor, the amorphous silicon surface is seeded. In the illustrated embodiment, the temperature is raised to a level within the range of about 550.degree. C. to 575.degree. C. (e.g., about 560.degree. C.) while the reactor pressure is preferably reduced to on the order of about 10.sup.-5 Torr. A seeding gas in the preferred embodiment is monosilane, provided with a silane partial pressure of about 4.times.10.sup.-6 Torr. After seeding, the density of which can be varied according to design, continued thermal treatment at the desired temperature results in a redistribution of mobile amorphous silicon. Silicon atoms tend to agglomerate about the seed or nucleation sites formed by the silane. The entire process takes on the order of about 10 minutes and 120 minutes for the batch system, including temperature ramp, seeding and anneal. The skilled artisan will readily appreciate numerous other techniques for forming HSG silicon.

Detail Description Paragraph - DETX (19):

[0054] If necessary, the exposed surfaces of the bottom electrode (e.g., the HSG silicon of the preferred embodiments) are terminated 102 to react with the first phase of the ALD process. The first phases of the preferred metal oxide embodiments (see Tables I to V) are reactive, for example, with hydroxyl (OH) or ammonia (NH.sub.3) termination. In the examples discussed below, silicon surfaces of HSG silicon will not generally require a separate termination. Exposure to a clean room environment results in native oxide formation that naturally provides OH termination 102. Where HSG is formed in situ or in a cluster tool prior to dielectric formation, it may be desirable to expose the HSG to H.sub.2O vapor, for example, as a surface preparation or termination 102 treatment. In other arrangements (see the discussion of Tables II and III below and FIG. 8), metal oxides can also be formed directly on silicon nitride without a separate termination step. In other words, nitridation of HSG silicon can serve as the termination 102.

Detail Description Paragraph - DETX (21):

[0056] The metal-containing reactive species is preferably supplied in

gaseous form, and is accordingly referred to hereinbelow as a metal source gas. The first chemistry is then removed 106 from the reaction chamber. In the illustrated embodiments, step 106 merely entails stopping the flow of the first chemistry while continuing to flow a carrier gas for a sufficient time to diffuse or purge excess reactants and reactant by-products out of the reaction chamber, preferably with greater than about two reaction chamber volumes of the purge gas, more preferably with greater than about three chamber volumes. In the illustrated embodiment, the removal 106 comprises continuing to flow purge gas for between about 0.1 seconds and 20 seconds after stopping the flow of the first chemistry. Inter-pulse purging is described in co-pending U.S. patent application having Ser. No. 09/392,371, filed Sep. 8, 1999 and entitled IMPROVED APPARATUS AND METHOD FOR GROWTH OF A THIN FILM, the disclosure of which is incorporated herein by reference. In other arrangements, the chamber may be completely evacuated between alternating chemistries. See, for example, PCT publication number WO 96/17107, published Jun. 6, 1996, entitled METHOD AND APPARATUS FOR GROWING THIN FILMS, the disclosure of which is incorporated herein by reference. Together, the adsorption 104 and removal 106 of excess reactant and by-products represent a first phase in an ALD cycle.

Detail Description Paragraph - DETX (24):

[0059] Desirably, the reaction 108 is also self-limiting. Reactants saturate the limited number of reaction sites left by step 104. Temperature and pressure conditions are preferably arranged to avoid diffusion of reactants from the second chemistry through the monolayer to underlying materials. The second chemistry also leaves a surface termination that is not reactive with excess reactants in the second chemistry, thus operating to limit the deposition in a saturative reaction phase. In the illustrated embodiments of Tables I to V below, hydroxyl (OH) tails and oxygen bridge termination on a metal oxide monolayer are non-reactive with excess oxygen source gases of the second chemistry.

Detail Description Paragraph - DETX (25):

[0060] After a time period sufficient to completely saturate the surface of the metal-complex monolayer through chemisorption (or self-limiting reaction) of the second chemistry, the excess second chemistry is removed 110 from the workpiece. As with the removal 106 of the first chemistry, this step 110 preferably comprises stopping the flow of the second chemistry and continuing to flow carrier gas for a time period sufficient to purge excess reactants and reaction by-products of the second chemistry from the reaction chamber. For example, reactants and reaction by-products can be removed by flowing purge gas

after stopping the flow of the first chemistry, preferably with at least about two chamber volumes of purge gas and more preferably with at least about three chamber volumes. In the illustrated embodiment, the removal 110 comprises continuing to flow purge gas for between about 0.1 seconds and 20 seconds after stopping the flow of the first chemistry. Together, the reaction 108 and removal 110 represent a second phase 111 in an ALD cycle.

Detail Description Paragraph - DETX (26):

[0061] In the illustrated embodiment, where two phases are alternated once the excess reactants and by-products of the second chemistry have been purged from the reaction chamber, the first phase of the ALD process is repeated. Accordingly, supplying 104 the first chemistry again to the workpiece forms another self-terminating monolayer.

Detail Description Paragraph - DETX (27):

[0062] The two phases 107, 111 thus represent a cycle 115 repeated to form monolayers in an ALD process. The first chemistry generally reacts (in a ligand-exchange) with or chemisorbs upon the termination left by the second chemistry in the previous cycle. If necessary, the cycle 115 can be extended to include a distinct surface preparation, similar to step 102, as shown in dotted lines in FIG. 4. The cycle 115 then continues through steps 104 to 110. This cycle 115 is repeated a sufficient number of times to produce a dielectric layer over the HSG silicon of a thickness sufficient to avoid current leakage during circuit operation. Alternatively, a thinner layer can be followed by further dielectric layers, deposited by a similar ALD process, to form a stack of dielectric sublayers, as will be better understood from the discussion of FIG. 9 below.

Detail Description Paragraph - DETX (29):

[0064] The illustrated cycle 215 of FIG. 4B, however, extends to include two additional phases. The first phase 207 and second phase 211 form a self-terminated metal oxide or silicon oxide monolayer. A third phase 219 and fourth phase 223 form another self-terminated metal oxide or silicon oxide monolayer. Note that the composition of the second monolayer preferably differs from the composition of the first monolayer at the discretion of the recipe designer. See, e.g. the metal silicate example of Table VI below.

Detail Description Paragraph - DETX (30):

[0065] In particular, after a first metal/silicon phase 207 and first oxygen phase 211 form a first metal oxide or silicon oxide monolayer, a second metal or silicon source gas is supplied 216 to form a self-limiting or self-terminating metal or silicon complex monolayer over the previously formed

metal/silicon oxide. Similar to the first metal/silicon phase 207, the metal/silicon gas source can react by ligand-exchange (chemisorption) upon the previously formed metal/silicon oxide. Following another removal 218 (by evacuation or preferably by purging) of the reactants, a second oxygen gas source is supplied 220 and then removed 222. The second oxygen step 220 (or oxygen phase 223) is also self-limiting. As with the first oxygen step 208, the oxygen gas source can react by ligand-exchange (chemisorption).

Detail Description Paragraph - DETX (32):

[0067] The second metal/silicon source gas in the third phase 219 can be a metal halide or metallorganic precursor, producing a metal complex monolayer self-terminated with halide or organic ligands that are non-reactive with the second metal/silicon source gas. In the example of Table VI, however, the second metal/silicon source gas comprises a silicon source gas conducive to self-limiting chemisorption, such as 3-aminopropyltriethoxysilane (NH.sub.2CH.sub.2CH.sub.2CH.sub.2--Si(O--CH.sub.3).sub.3 or AMTES) or 3-aminopropyltrimethoxysilane (NH.sub.2CH.sub.2CH.sub.2CH.sub.2--Si(O--CH.sub.3).sub.3 or AMTMS) compound, or a halosilane. Note that the sequence of the metal source and silicon source phases can be reversed.

Detail Description Paragraph - DETX (33):

[0068] The oxygen source gas of the fourth phase 220 can be the same or differ from that of the second phase 211. The inventors have found certain oxidants (e.g., ozone) to be advantageous for oxidizing metal or silicon complex monolayers having organic ligands, whereas other oxidants (e.g., water) are more advantageous for halide-terminated metal or silicon complex monolayers. Accordingly, in the example of Table VI below, the oxidant of the fourth phase 223 differs from the oxidant of the third phase 219, at least for those cycles in which the metal/silicon source of the third phase 219 differs from the metal/silicon source of the first phase 207.

Detail Description Paragraph - DETX (42):

[0077] During the pulse 104, the metal source gas reacts with exposed surfaces of the workpiece to deposit or chemisorb a "monolayer" of metal complex. While theoretically the reactants will chemisorb at each available site on the exposed layer of the workpiece, physical size of the adsorbed complex (particularly with large terminating ligands) will generally limit coverage with each cycle to a fraction of a monolayer. In the example of Table I, the ALD process grows metal oxide layers at roughly 1 .ANG./cycle, such that

a full monolayer effectively forms from material deposited approximately every 3 cycles for Al.sub.2O.sub.3, which has a bulk lattice parameter of about 3 .ANG.. Each cycle is represented by a pair of metal source gas and oxygen source gas pulses. "Monolayer," as used herein, therefore represents a fraction of a monolayer during deposition, referring primarily to the self-limiting effect of the pulse 104.

Detail Description Paragraph - DETX (43):

[0078] In particular, the metal-containing species provided to the workpiece is self-terminating such that the adsorbed complex surface will not further react with the metal source gas. In the examples set forth below, TMA (Table I) leaves a monolayer of methyl-terminated aluminum. Tantalum ethoxide (Table II) leaves a monolayer of ethoxide tantalum. Similarly, other volatile metal halides will leave halide-terminated surfaces, and metallorganic precursors will leave surface terminated with organic ligands. Such surfaces do not further react with the metal source or other constituents of the reactant flow during the metal source gas pulse 104. Because excess exposure to the reactants does not result in excess deposition, the chemistry during the metal phase 107 of the process is said to be saturative or self-limiting. Despite longer exposure to a greater concentration of reactants, deposition on upper surfaces of HSG silicon grains does not exceed deposition in neck regions between grains

Detail Description Paragraph - DETX (44):

[0079] In a second phase 111 of the cycle 115, a pulse 108 of an oxygen source gas is then provided to the workpiece. In the illustrated examples, the oxygen source gas comprises water vapor (H.sub.2O) or ozone. Other suitable oxidants include: hydrogen peroxide (H.sub.2O.sub.2); methanol (CH.sub.3OH); ethanol (CH.sub.3CH.sub.2OH), nitrous oxide (N.sub.2O, NO.sub.2); O radicals; etc. Radicals can be provided by remote plasma sources connected to the reaction chamber, and an ozone generator can similarly provide ozone (O3). Preferably, the second phase 111 is maintained for sufficient time to fully expose the monolayer of metal complex left by the first phase 107 to the oxygen source gas. After a sufficient time for the oxygen source gas to saturate the metal-containing monolayer over the HSG silicon layer, shutting off the flow of the oxygen source gas ends the oxygen pulse 108. Preferably, carrier gas continues to flow in a purge step 110 until the oxygen source gas is purged from the chamber.

Detail Description Paragraph - DETX (46):

[0081] In particular, the oxygen source gas reacts with the ligand of the metal complex chemisorbed onto the workpiece surface during the previous pulse

of metal source gas. The reaction is also surface limiting or terminating, since the oxidant during the pulse 108 will not react with the hydroxyl and oxygen bridge termination of the metal oxide monolayer. Moreover, temperature and pressure conditions are arranged to avoid diffusion of the oxidant through the metal monolayer to underlying materials. Despite longer exposure to a greater concentration of reactants in this saturative, self-limiting reaction phase 111, the thickness of the metal oxide formed on upper surfaces of the HSG silicon grains does not exceed the thickness of the metal oxide formed in the neck regions between grains.

Detail Description Paragraph - DETX (47):

[0082] The metal phase 107 (including metal source pulse 104 and purge 106) and oxygen phase 108 (including oxygen source pulse 108 and purge 110) together define a cycle 15 that is repeated in an ALD process. After the initial cycle 115, a second cycle 115a is conducted, wherein a metal source gas pulse 104a is again supplied. The metal source gas chemisorbs a metal complex on the surface of the metal oxide formed in the previous cycle 115. The metal-containing species readily react with the exposed surface, depositing another monolayer or fraction of a monolayer of metal complex and again leaving a self-terminated surface that does not further react with the metal source gas. Metal source gas flow 104a is stopped and purged 106a from the chamber, and a second phase 111a of the second cycle 115a provides oxygen source gas to oxidize the second metal monolayer.

Detail Description Paragraph - DETX (49):

[0084] The tables below provide exemplary process recipes for forming metal oxide and ternary dielectric layers suitable for capacitor dielectric applications in DRAM memory cells for ultra large scale integrated processing. The dielectrics are particularly suited to deposition over HSG silicon. Each of the process recipes represents one cycle in a single-wafer process module. In particular, the illustrated parameters were developed for use in the single-wafer ALD module commercially available under the trade name Pulsar 2000.TM., available commercially from ASM Microchemistry Ltd. of Finland.

Detail Description Paragraph - DETX (50):

[0085] Note that the parameters in the tables below are exemplary only. Each process phase is desirably arranged to saturate the bottom electrode surfaces. Purge steps are arranged to remove reactants between reactive phases from the reaction chamber. The illustrative ALD processes achieve better than about 95% thickness uniformity, and more preferably greater than about 98% thickness uniformity over HSG grains with average grain sizes of about 400 .ANG.. Thickness uniformity, as used herein, is defined as the percentage of a

thickness minimum as a percentage of the thickness maximum. In view of the disclosure herein, the skilled artisan can readily modify, substitute or otherwise alter deposition conditions for different reaction chambers and for different selected conditions to achieve saturated, self-terminating phases at acceptable deposition rates.

Detail Description Paragraph - DETX (51):

[0086] Advantageously, the ALD processes described herein are relatively insensitive to pressure and reactant concentration, as long as the reactant supply is sufficient to saturate the textured surfaces. Furthermore, the processes can operate at low temperatures. Workpiece temperature is preferably maintained throughout the process between about 150.degree. C. and 350.degree. C. to achieve relatively fast deposition rates while conserving thermal budgets. More preferably, the temperature is maintained between about 220.degree. C. and 300.degree. C., depending upon the reactants. Pressure in the chamber can range from the milliTorrrange to super-atmospheric, but is preferably maintained between about 1 Torr and 500 Torr, more preferably between about 1 Torr and 10 Torr.

Detail Description Paragraph - DETX (52):

[0087] Table I above presents parameters for ALD of an aluminum oxide (Al.sub.2O.sub.3) dielectric over HSG silicon. The exemplary metal source gas comprises trimethyl aluminum (TMA), the carrier gas comprises nitrogen (N.sub.2) and the oxygen source gas preferably comprises water vapor (H.sub.2O). The temperature during the process is preferably kept between about 150.degree. C. and 350.degree. C., and more preferably at about 300.degree. C.

Detail Description Paragraph - DETX (54):

[0089] After the TMA flow is stopped and purged by continued flow of carrier gas, a pulse of H.sub.2O is supplied to the workpiece. The water readily reacts with the methyl-terminated surface of the metal monolayer in a ligand-exchange reaction, forming a monolayer of aluminum oxide (Al.sub.2O.sub.3). The reaction is limited by the number of available metal complexes previously chemisorbed. The reaction is furthermore self-limiting in that neither water nor the carrier gas further reacts with the hydroxyl and oxygen bridge termination of the resulting aluminum oxide monolayer. The preferred temperature and pressure parameters, moreover, inhibit diffusion of water or reaction by-products through the metal monolayer.

Detail Description Paragraph - DETX (57):

[0092] Radicals provided by plasma generators can facilitate deposition of

metal-containing layers at the low temperatures of ALD processing. Structures and methods of depositing layers with radical enhancement are provided in patent application having Ser. No. 09/392,371, filed Sep. 8, 1999 and entitled IMPROVED APPARATUS AND METHOD FOR GROWTH OF A THIN FILM, the disclosure of which is incorporated by reference hereinabove. Another exemplary ALD process flow is provided in U.S. Pat. No. 5,916,365 to Shermnan, issued Jun. 29, 1999, the disclosure of which is incorporated herein by reference.

Detail Description Paragraph - DETX (58):

[0093] Table II above presents parameters for ALD of a tantalum oxide (Ta.sub.2O.sub.5) over HSG silicon of a capacitor bottom electrode. Preferably, the illustrated dielectric deposition is preceded by formation of a barrier layer to protect the HSG silicon from oxidation. In the illustrated embodiment, a dielectric barrier is formed, specifically comprising silicon nitride (Si.sub.3N.sub.4). Advantageously, silicon nitride can be formed over HSG silicon with near perfect conformality by thermally nitriding the silicon surfaces. In other arrangements, a thin oxide layer can be first grown (e.g., by thermal oxidation) over the HSG silicon, followed by thermal nitridation of the oxide surface, as is known in the art.

Detail Description Paragraph - DETX (59):

[0094] Following formation of the barrier layer, Ta.sub.2O.sub.5 is formed in an ALD process. As indicated in Table II, the illustrated metal source gas comprises tantalum ethoxide (Ta(OCH.sub.2CH.sub.3).sub.5); the carrier gas comprises nitrogen (N.sub.2); and the oxygen source gas preferably comprises ozone (O.sub.3). The temperature during the process is preferably kept between about 150.degree. C. and 300.degree. C., and more preferably at about 220.degree. C.

Detail Description Paragraph - DETX (61):

[0096] After the metal source gas flow is stopped and purged by continued flow of carrier gas, a pulse of ozone is supplied to the workpiece. Ozone preferably comprises a sufficient percentage of the carrier flow, given the other process parameters, to saturate the surface of the metal-containing monolayer. The ozone readily reacts with the ethoxide-terminated surface of the metal-containing monolayer in a ligand-exchange reaction, forming a monolayer of tantalum oxide (Ta.sub.2O.sub.5). The reaction is limited by the number of available metal complexes previously chemisorbed. Neither ozone nor the carrier gas further reacts with the resulting tantalum oxide monolayer. Ozone causes the organic ligand to burn, liberating CO.sub.2 and H.sub.2O, and the monolayer is left with hydroxyl and oxygen bridge termination. The

preferred temperature and pressure parameters, moreover, inhibit diffusion of ozone and reaction by-products through the metal monolayer.

Detail Description Paragraph - DETX (65):

[0100] Table III above presents parameters for another ALD process for depositing tantalum oxide (Ta.sub.2O.sub.5) over HSG silicon of a capacitor bottom electrode. Following formation of the silicon nitride barrier layer, as described above, Ta.sub.2O.sub.5 is formed in an ALD process. As indicated in Table III, the preferred metal source gas comprises tantalum chloride (TaCl.sub.5); the carrier gas again comprises nitrogen (N.sub.2); and the oxygen source gas preferably comprises water vapor (H.sub.2O). Temperatures during the process are preferably between about 150.degree. C. and 300.degree. C., and more preferably about 300.degree. C.

Detail Description Paragraph - DETX (67):

[0102] After the TaCl.sub.5 flow is stopped and purged by continued flow of carrier gas, a pulse of water vapor is supplied to the workpiece. Water vapor preferably comprises a sufficient percentage of the carrier flow, given the other process parameters, to saturate the surface of the metal-containing monolayer. The water readily reacts with the chloride-terminated surface of the metal-containing monolayer in a ligand-exchange reaction, forming a monolayer of tantalum oxide (Ta.sub.2O). The reaction is limited by the number of available metal chloride complexes previously chemisorbed. Neither water nor the carrier gas further reacts with the hydroxyl and oxygen bridge termination of the resulting tantalum oxide monolayer. The preferred temperature and pressure parameters, moreover, inhibit diffusion of water and reaction by-products through the metal monolayer.

Detail Description Paragraph - DETX (71):

[0106] Table IV above presents parameters for ALD of zirconium oxide (ZrO.sub.2). As noted, the metal source comprises zirconium chloride (ZrCl.sub.4); the carrier gas comprises nitrogen (N.sub.2); and the oxygen source gas preferably comprises water vapor (H.sub.2O). During each of the reaction phases, the reactants are supplied in sufficient quantity for the given other parameters to saturate the surface. Temperatures during the process preferably fall between about 200.degree. C. and 500.degree. C. For an amorphous ZrO.sub.2 layer, the temperature is more preferably at the low end of this range, between about 200.degree. C. and 250.degree. C., and most preferably at about 225.degree. C. For a crystalline film, the temperature is more preferably at the high end of this range, between about 250.degree. C. and 500.degree. C., and most preferably about 300.degree. C. As will be appreciated by the skilled artisan, however, mixtures of amorphous and

crystalline composition result at the boundary of these two regimes. The illustrated process produces a largely crystalline ZrO.sub.2 film.

Detail Description Paragraph - DETX (74):

[0109] Table V above presents parameters for ALD of titanium oxide (TiO.sub.2). As noted, the metal source comprises titanium tetrachloride (TiCl.sub.4); the carrier gas comprises nitrogen (N.sub.2); and the oxygen source gas preferably comprises water vapor (H.sub.2O). During each of the reaction phases, the reactants are supplied in sufficient quantity for the given other parameters to saturate the surface.

Detail Description Paragraph - DETX (75):

[0110] As described with respect to ZrO.sub.2 in the preceding example, temperatures is preferably kept at a level between about 200.degree. C. and 500.degree. C. In the illustrated embodiment, however, the illustrated embodiment employs a temperature between about 250.degree. C. and 500.degree. C., and most preferably about 300.degree. C.

Detail Description Paragraph - DETX (79):

[0114] As discussed with respect to FIG. 4B, the principles of ALD described above with respect to metal oxide capacitor dielectrics, can also be extended to depositing ternary materials and more complex materials.

Detail Description Paragraph - DETX (82):

[0117] In general, the process enables dielectric layers having mixed metal oxides, ternary metal oxide compounds, metal silicates, or more complex dielectric materials. For example, TiO.sub.2 can be mixed with Ta.sub.2O.sub.5 by alternating cycles. A largely binary cycle can be repeated several times between ternary cycles, if only a slight doping effect is desired. The example of Table VI below, however, a zirconium silicon oxide or "zirconium silicate" layer is illustrated.

Detail Description Paragraph - DETX (83):

[0118] Table VI above presents parameters for ALD of zirconium silicon oxide or zirconium silicate (ZrSi.sub.xO.sub.y). As noted in Table VI, the first reactant source comprises a source of metal for the compound to be formed. In particular, zirconium chloride (ZrCl.sub.4) supplies the metal. Other process gases include the carrier gas, comprising nitrogen (N.sub.2) in the illustrated embodiment, and a silicon source gas, preferably comprising 3-aminopropyltrimethoxysilane (NH.sub.2CH.sub.2CH.sub.2CH.sub.2--Si(O--CH.sub.3).sub.3 or AMTMS). Other suitable silicon gas sources include various organosilane and halosilane gases.

During each of the reaction phases, the reactants are supplied in sufficient quantity for the given other parameters to saturate the surface.

Detail Description Paragraph - DETX (85):

[0120] During the metal phase, a zirconium-containing monolayer is self-terminated with chloride tails. The termination of this monolayer does not readily react with ZrCl_4 under the preferred conditions. In the next phase, water vapor oxidizes the metal containing monolayer, replacing chloride termination with hydroxyl and oxygen bridge termination. Then the preferred silicon source gas reacts with or adsorbs upon the hydroxyl and oxygen bridge termination during the silicon phase in a ligand-exchange reaction limited by the supply of metal oxide complexes previously adsorbed. Moreover, the preferred silicon source gas leaves an organic (ethoxide) or halide (chloride) termination that does not further react with excess silicon ethoxide in the saturative phase. Finally, ozone oxidizes the previously adsorbed silicon-containing monolayer to leave a ternary oxide.

Detail Description Paragraph - DETX (90):

[0125] Preferably at least one of the sublayers, and more preferably all of the sublayers, is formed by ALD in accordance with the methods disclosed above. FIG. 9 illustrates an exemplary capacitor formed by this process, discussed in more detail below.

Detail Description Paragraph - DETX (94):

[0129] After formation of the dielectric layer, a top electrode is formed over the capacitor dielectric. If the top electrode does not perfectly conform to the dielectric, the full benefit of the textured bottom electrode and conformal dielectric is not realized. Accordingly, the top electrode formed over the capacitor dielectric preferably includes at least one conductive thin film that is also deposited with near perfect conformality by an ALD process.

Detail Description Paragraph - DETX (97):

[0132] In the example of Table VII below, the top electrode comprises a conductive metal nitride, which can serve as a barrier layer over Ta_2O_5 , deposited by an ALD process to conformally and continuously coat the capacitor dielectric. The example of Table VIII below the top electrode comprises an elemental metal layer, which can overlie or replace the barrier of Table VII, also formed by an ALD process.

Detail Description Paragraph - DETX (98):

[0133] Table VII above presents parameters for ALD of a conformal metal nitride barrier over a capacitor dielectric. The process is similar to that of

FIGS. 4A and 5, except that the oxygen source gas is substituted with a nitrogen source gas. Accordingly, one of the reactant species preferably includes a metal-containing species with an organic or halide ligand, while a second reactant species includes a nitrogen-containing species. In the illustrated embodiment, the metal film comprises a titanium nitride (TiN) film formed by ALD in alternating, self-limiting metal and nitrogen phases separated by purge steps. In the example of Table VII, the exemplary metal source gas comprises titanium tetrachloride (TiCl.sub.4), the carrier gas comprises nitrogen (N.sub.2) and the nitrogen source gas preferably comprises ammonia (NH.sub.3).

Detail Description Paragraph - DETX (101):

[0136] After the TiCl.sub.4 flow is stopped and purged by continued flow of carrier gas, a pulse of NH.sub.3 is supplied to the workpiece. Ammonia preferably comprises a sufficient percentage of the carrier flow, given the other process parameters, to saturate the surface of the metal-containing monolayer. The NH.sub.3 readily reacts with the chloride-terminated surface of the metal monolayer in a ligand-exchange reaction, forming a monolayer of titanium nitride (TiN). The reaction is limited by the number of available metal chloride complexes previously chemisorbed. Neither ammonia nor the carrier gas further reacts with the resulting titanium nitride monolayer. The preferred temperature and pressure parameters, moreover, inhibit diffusion of ammonia through the metal monolayer.

Detail Description Paragraph - DETX (104):

[0139] Table VIII above presents parameters for ALD of a conformal elemental metal layer over a capacitor dielectric. The process can be conducted immediately following formation of a barrier layer (see Table VII) or directly over the capacitor dielectric. The process is also similar to that of FIGS. 4A and 5, except that the oxygen source gas is substituted with a reducing agent. Accordingly, one of the reactant species preferably includes a metal-containing species with an organic or halide ligand, while a second reactant species includes a strong reducing agent. In the illustrated embodiment, the metal film comprises a tungsten (W) layer formed by ALD, in alternating metal and reducing phases separated by purge steps. In the example of Table VIII, the metal source gas comprises tungsten hexafluoride (WF.sub.6), the carrier gas comprises nitrogen gas (N.sub.2) and the reducing agent comprises triethyl boron ((CH.sub.3CH.sub.2).sub.3B) or TEB.

Detail Description Paragraph - DETX (106):

[0141] After the WF.sub.6 flow is stopped and purged by continued flow of carrier gas, a pulse of TEB is supplied to the workpiece. TEB preferably

comprises a sufficient percentage of the carrier flow, given the other process parameters, to saturate the surface of the metal-containing monolayer. The TEB readily reduces the halide-terminated surface of the metal-containing monolayer, leaving a monolayer of tungsten. The number of available metal halide complexes previously chemisorbed limits the reaction. Neither TEB nor the carrier gas further reacts with the resulting tungsten monolayer. The preferred temperature and pressure parameters, moreover, inhibit diffusion of TEB through the metal monolayer.

Detail Description Paragraph - DETX (109):

[0144] Following ALD formation of the initial conductive thin film(s), preferably by process(es) similar to that of Table VII and/or Table VIII, conventional deposition processes can form the remainder of the top electrode. CVD and even PVD can be utilized to deposit an additional 100 nm to 500 nm of conductive material. Conventional deposition will not generally coat the initial thin film(s) with high step coverage, and therefore will not conform with precision to the underlying texture imposed by the bottom electrode and extended by the highly conformal dielectric and initial conductive thin films. Imperfect step coverage by the bulk deposition, however, will not result in loss of capacitance, since the initial conductive thin film(s) ensure continuous and conformal coverage of the capacitor dielectric by a portion of the top electrode.

Detail Description Paragraph - DETX (117):

[0152] Referring now to FIG. 10, a capacitor bottom electrode 300, including HSG silicon 304, has an ultrathin, high k dielectric 302 conforming thereto, as described with respect to FIG. 7. Additionally, FIG. 10 illustrates a top electrode formed over the high k dielectric 302. Advantageously, the top electrode includes an initial conductive thin film 308, formed by ALD directly over the high k dielectric. Since the conductive thin film 308 is deposited by the ALD process described with respect to Table VII and/or Table VIII, the conductive layer 308 conformally coats the capacitor dielectric, thus ensuring full top electrode coverage of the high surface capacitor. At the same time, a remaining portion 310 of the top electrode can be formed by conventional means, such as CVD or PVD, without loss of capacitance.

Detail Description Paragraph - DETX (120):

[0155] Although the foregoing invention has been described in terms of certain preferred embodiments, other embodiments will be apparent to those of ordinary skill in the art. For example, while processes are specifically provided for particular dielectric materials, the skilled artisan will readily appreciate that ALD methods can be applied to forming capacitors with other

materials. Moreover, although illustrated in connection with particular process flows and structures for memory cell capacitors, the skilled artisan will appreciate variations of such schemes for which the methods disclosed herein will have utility. Additionally, other combinations, omissions, substitutions and modification will be apparent to the skilled artisan, in view of the disclosure herein. Accordingly, the present invention is not intended to be limited by the recitation of the preferred embodiments, but is instead to be defined by reference to the appended claims.

Detail Description Table CWU - DETL (1):

1TABLE I Al.sub.2O.sub.3 Carrier Reactant Flow Flow Temperature Pressure
Time Phase (sccm) Reactant (sccm) (.degree. C.) (Torr) (sec) metal 400 TMA
20 300 5 0.1 purge 400 -- -- 300 5 0.2 oxidant 400 H.sub.2O 40 300 5 0.1
purge 400 -- -- 300 5 0.6

Detail Description Table CWU - DETL (3):

3TABLE III Ta.sub.2O.sub.5 Carrier Reactant Flow Flow Temperature
Pressure Time Phase (sccm) Reactant (sccm) (.degree. C.) (Torr) (sec) metal
400 TaCl.sub.5 40 300 5 0.5 purge 400 -- -- 300 5 0.5 oxidant 400 H.sub.2O 40
300 5 0.5 purge 400 -- -- 300 5 0.5

Detail Description Table CWU - DETL (4):

4TABLE IV ZrO.sub.2 Carrier Reactant Flow Flow Temperature Pressure Time
Phase (sccm) Reactant (sccm) (.degree. C.) (Torr) (sec) metal 400 ZrCl.sub.4
5 300 5 0.5 purge 400 -- -- 300 5 3 oxidant 400 H.sub.2O 40 300 5 2 purge
400 -- -- 300 5 6

Detail Description Table CWU - DETL (5):

5TABLE V TiO.sub.2 Carrier Reactant Flow Flow Temperature Pressure Time
Phase (sccm) Reactant (sccm) (.degree. C.) (Torr) (sec) metal 400 TiCl.sub.4
20 300 5 0.5 purge 400 -- -- 300 5 3 oxidant 400 H.sub.2O 40 300 5 2 purge
400 -- -- 300 5 6

Detail Description Table CWU - DETL (6):

6TABLE VI Zirconium silicon oxide Carrier Reactant Flow Flow Temperature
Pressure Time Phase (sccm) Reactant (sccm) (.degree. C.) (Torr) (sec) metal
400 ZrCl.sub.4 40 300 5 0.5 purge 400 -- -- 300 5 3 oxygen 400 H.sub.2O 40
300 5 2 purge 400 -- -- 300 5 6 silicon 400 AMTMS 40 300 5 1 purge 400 -- --
300 5 2 oxygen 400 O.sub.3 40 300 5 3.5 purge 400 -- -- 300 5 1

Detail Description Table CWU - DETL (7):

7TABLE VII TiN Carrier Reactant Flow Flow Temperature Pressure Time

Phase (sccm) Reactant (sccm) (.degree. C.) (Torr) (sec) metal 400 TiCl.sub.4
 20 400 10 1 purge 400 --- 400 10 1 nitrogen 400 NH.sub.3 100 400 10 2
 purge 400 --- 400 10 4

Detail Description Table CWU - DETL (8):

8TABLE VIII Carrier Reactant Flow Flow Temperature Pressure Time Phase
 (sccm) Reactant (sccm) (.degree. C.) (Torr) (sec) metal 600 WF.sub.6 50 400
 10 0.25 purge 600 --- 400 10 0.5 reduce 600 TEB 40 400 10 0.1 purge 600
 --- 400 10 0.8

Claims Text - CLTX (13):

12. The method of claim 11, wherein the dielectric layer is selected from the group consisting of aluminum oxide, tantalum oxide, titanium oxide, zirconium oxide, niobium oxide, hafnium oxide, silicon oxide and mixtures and compounds thereof.

Claims Text - CLTX (23):

22. The method of claim 20, wherein forming a barrier layer comprises oxidizing the textured silicon surface to form a silicon oxide and nitriding the silicon oxide.

Claims Text - CLTX (51):

50. An integrated circuit having a plurality of memory cells, each memory cell including a capacitor comprising: a first electrode having a surface conforming to a hemispherical grain morphology; a capacitor dielectric layer adjacent to the first electrode and conforming to the hemispherical grain morphology, the capacitor dielectric comprising a material selected from the group consisting of aluminum oxide, titanium oxide, zirconium oxide, niobium oxide, hafnium oxide, silicon oxide and mixtures and compounds thereof; and a second electrode adjacent to and conforming to the hemispherical grain morphology.

Claims Text - CLTX (63):

62. The process of claim 55, comprising maintaining a temperature of less than about 350.degree. C.